



Highly constrained guests in complexes of *p*-*tert*-butylcalix[6]arene dianion: Pentane-1,5-diammonium and choline



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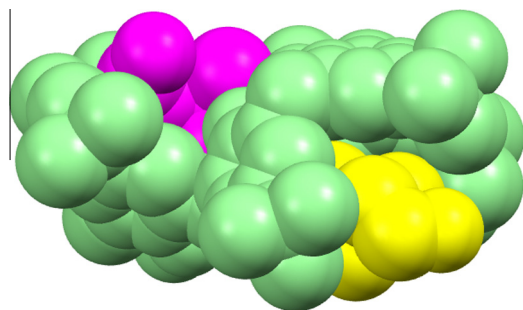
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GRAPHICAL ABSTRACT

Two choline units (yellow and pink) deep immersed in the cavity of *p*-*t*-bu-calix[6]arene dianion (light green).



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ABSTRACT

The structures of the complexes of choline and pentane-1,5-diammonium with *p*-*t*-bu-calix[6]arene dianion were determined. Both salts display the calixarene moiety at 1,2,3-alternate conformation, with two concave surfaces formed by three aromatic rings, and the phenolate units are at distal positions, interacting with two phenol units by hydrogen bonds.

The salt of pentane-1,5-diammonium shows the diammonium connecting both calixarene dianion units, and one NH_3^+ is located *endo*-calix position and the other occupies an *exo*-calix position. The *t*-butyl groups and the calix cavity constrains the pentane-1,5-diammonium chain to near *syn-eclipsed* and *gauche* conformations. The other semi-calix accomodates a THF solvent molecule. The salt of choline shows the trimethylammonium groups of choline units immersed in these concave surfaces, with several interactions $\text{N}^+-\text{C}-\text{H}-\pi$ interactions with the aromatic semi-cavities.

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Introduction

Calixarene based receptors are able to interact with organic and inorganic molecules and ions [1], and the interactions with

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biomolecules [2–4] have special interest for sensors and carriers, which increase the solubility of bioactive molecules [5] and allow the controlled delivery of pharmaceuticals.

The aromatic cavity of calixarenes **1** (Fig. 1) is able to interact by π stacking and $\text{C}-\text{H}-\pi$ from one side [6] and the phenolic hydroxyl groups interact by hydrogen bonds or electrostatic by the other side [7]. The complexes of calix[6]arene with ammonium cations

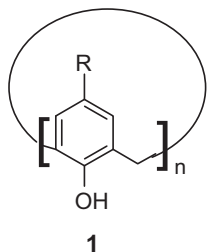


Fig. 1. General structure of a calix[n]arene.

have been described with 2:1 ammonium: calix stoichiometry. The relative position of ammonium complexes of calix[6]arene salts is related with the size complementarity of the cation and the cavity. Tetramethylammonium cation complexes have both cations placed *endo*-calix [8], whereas the bis-hexylammonium [9] salt have one ammonium in the *endo*-calix and the other *exo*-calix positions. Bulkier ammonium cations like triethylammonium have both ammonium units placed out of the cavity of calix[6]arene [10].

Choline and acetylcholine are neurotransmitters acting in the nervous central systems, which can be considered important targets for molecular recognition by their role on the enhancing of cation transport in cation channels and their esters are in the surface of cellular membranes. Signal deactivation is mediated by acetylcholinesterase (AChE) enzymes, which are targets for insecticides, and their irreversible inactivation kills by neuromuscular paralysis [11]. The recognition of the trimethylcation moiety in acetylcholinesterase from *torpedo californica* [12] and choline oxidase from *sinorhizobium meliloti* [13] is provided by $N^+-CH_3-\pi$ interaction with residues of Tyr, Phe and Trp, and the affinity of the synthetic receptor sulphonate-calixarenes by choline was reported by Lehn et al. [14] as comparable with biological receptors, with one choline unit inside of the calix cavity. The binding of calixarene in the outer surface of membranes has been pointed as the possible reason for antibacterial properties of calix-guanidine derivatives [15]. This work describes the salts of *p-t*-bu-calix[6]arene dianion with two ammonium cations: pentane-1,5-diammonium (cadaverine diammonium) and choline in order to evaluate the main forces that control the complexation.

Experimental

The complex of pentane-1,5-diammonium and *p-t*-bu-calix[6]arene dianion was obtained from a solution of 1:1 mol ratio of *p-t*-bu-calixarene and pentane-1,5-diamine (cadaverine) from in

CH_3CN/THF . The suspension was heated and filtered, and the slow evaporation of the solvent mixture yielded colorless crystals. Crystals of calixarene dianion with choline were obtained by previous reaction of *p-t*-bu-calix[6]arene with KOH with a 1:2 mol ratio in ethanol. Subsequent addition of choline chloride until 10:1 choline: calix ratio, yielded colorless crystals after two days.

Data were collected on an Enraf–Nonius Kappa-CCD diffractometer with graphite monochromated Mo K radiation ($\lambda = 0.71073 \text{ \AA}$), up to 50° in 2θ and final unit cell parameters were based on all reflections. The temperature was controlled using an Oxford Cryo-system low temperature device operating at 120 K. Data collection was carried out using the COLLECT program [16]. Integration and scaling of the reflections were performed with the HKL Denzo–Scalepack system of programs [17,18], and numerical absorption corrections were performed. The structure was solved using direct methods with SHELXS-97 [19]. The model was refined by full-matrix least-squares on F² by with SHELXL-97. Hydrogen atoms were located on stereochemical grounds and refined with the riding model; for methyl and phenolic hydrogens, the rotating model was used. Hydrogen atoms were set isotropic with a thermal parameter 20% greater than the equivalent isotropic displacement parameter of the carbon to which each one is bonded; this percentage was set to 50% for the hydrogen atoms of methyl groups. The infrared analysis of the salts were collected using a Varian 640-IR as KBr pellets.

Results and discussion

This work is part of our efforts to evaluate the forces involved in the complexation of ammonium cations with calixarenes, focusing in biomolecules. We also sought organized structures, where an diammonium cation is able to connect two calixarene units, so we tried to obtain crystals with 1,8 – 1,6 – 1,5 and 1,4 diammonium linear cations, and only the reaction with pentane-1,5-diammonium (cadaverine) shown in Fig. 2, yielded good crystals from a solution with 1:1 diamine: calix. We tried other calix: diamine molar ratios to grow crystals: 1:1, 1:2, 1:4 and 1:10, but only the first resulted crystals with good quality for X-ray analysis. The other ratios gave the 2:1 ammonium: calix, although none formed monocrystal with quality to X-ray analysis.

The synthesis of the choline came from our observations about the competition between quaternary ammonium cations and alkaline cations. In a first attempt, alkaline metal hydroxides were added to a suspension of *p-t*-bu-calix[6]arene, followed by the addition of tetramethylammonium chloride. The tetramethylammonium salt with the calixarene crystallized in all experiments performed, instead of the metal salt, as seen as seen by infrared analysis of the solids obtained. So, we used choline and

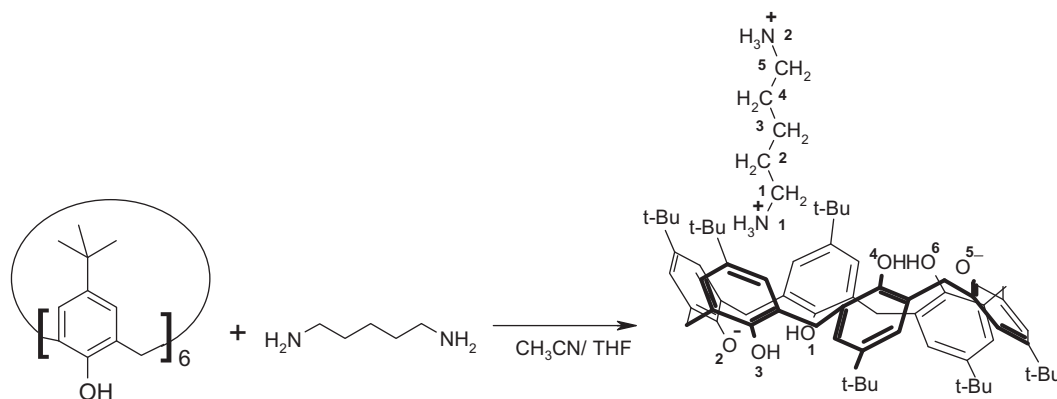


Fig. 2. Synthesis of the complex of *p-t*-bu-calix[6]arene dianion with pentane-1,5-diammonium.

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